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ELECTRICAL RESISTIVITY OF CARBON BLACK-  
KAOLIN SINTERED MATERIALS. II

Etsuro Kato

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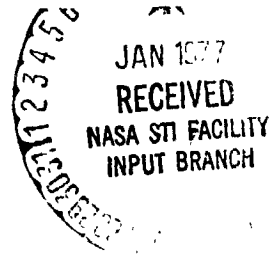
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| 16. Abstract<br>C solid resistors contg. furnace black < 15% in kaolin were made and fired at 800-1400° for 1 hr. The vol. contraction of the resistor occurs at 500° (due to dehydration), 1000° (destruction of metakaolin structure), and 1100° (pptn. of mullite and vitrefication). The elec. resistivity changes with the firing temp., corresponding to the vol. changes. When fired at <1300°, the log of the sp. resistance, $\rho$ , is linear with the reciprocal of the bulk C d., C, in the region of low $\rho$ , C being defined as the wt. of C in a unit vol. of the composite resistor. When fired at < 1300°, the deviation from such linearity is appreciable. These properties are not due to intrinsic changes in the properties of the 2 components by firing. The exptl. results can be reproduced by the formula $\rho = K \rho' \exp\{(k/C_0)(V/V_0) - \ln(V_0/V)\}^{-1}$ derived by a theoretical consideration; here K is a const., $\rho'$ is the sp. resistance of the C black, k is a const. unless $C_0$ is very small, $C_0$ is the value of C before firing, and $V_0$ and V are the vol. of the composite resistor before and after the firing. The formula is good below 1200° firing temp., above which other effects, including chem. reactions, begin to contribute. |  |  |           |
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# ELECTRICAL RESISTIVITY OF CARBON BLACK KAOLIN SINTERED MATERIALS II

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As basic research into the production of solid ceramic resistors, studies were made of the effects of calcination temperatures (800-1400° C) on resistivity and of the relation with changes in resistance of structural materials and calcined contraction. The comparative resistance of the sintered materials decreased in stages with rise in calcination temperature. These stages have a corresponding relation with the stages of change of calcined contraction but there is little relation with the resistance of the components. Considering the effects of calcined contraction and the compression on carbon black of the compound, the following formula was derived for resistance of sintered materials, using various other hypotheses.

$$\rho = K \cdot \rho' \cdot e^{k/C} \cdot \frac{1}{\sqrt{p}}$$

Using calcined contraction,

$$\rho = K' \cdot \rho' \cdot e^{\frac{k}{C_0} \cdot \frac{V}{V_0}} \cdot \left( -\ln \frac{V}{V_0} \right)^{-1/2}$$

Here K, K' are constant, p' is the specific resistance of carbon black, C<sub>0</sub> and C are the bulk densities of carbon before and after sintering, k is fixed when C is not too small and p is the pressure which carbon black receives in the sintered material.

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\*\*Numbers in margin refer to pagination of original foreign text.

The items  $e^{k/c}$  and  $1/\sqrt{p}$  are related to the points of contact and the areas of contact. This formula coincides closely with experimental results up to sintering temperature of 1200°C. When 1200°C is exceeded, although the effect beyond contraction appears (One is probably a chemical reaction), calcined contraction is believed to have the most basic effect on the resistance of sintered materials.

#### 1. Introduction

In the production of solid ceramic resistors, the calcination temperature has a final and decisive influence on the resistivity of the sintered material and this is closely related to the problem of yield in production. However, the nature of this influence is not yet known. Until now, only some qualitative studies have been conducted similar to those into various factors of production conditions prior to sintering<sup>1]</sup>.

In a previous report,<sup>2]</sup> the author found a clear correlation with sufficient reproducibility between the amount of carbon admixture and the resistance of sintered materials of carbon black and kaolin. Especially in the sphere of low resistance, when the carbon admixture amount is expressed as the admixture per unit area of sintered material computed from calcined contraction, specifically as bulk density (C) of sintered carbon §<sup>1</sup>, the clear relation of  $\rho = Ae^{k/c}$  (A and k are constants)  

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§<sup>1</sup> (C) will be the carbon bulk density of sintered material, differentiated from the carbon admixture rate (wt % in non-calcined dried sample).

is exhibited with the specific resistance ( $\rho$ ) of sintered material. This relation can be the basis for understanding the details of the effect of calcination temperature on resistivity and in the sense that  $C$  at least changes in the previous report, calcined contraction is important. However, the relative changes due to calcination temperature related to quantity. Specifically the changes in constants  $A$  and  $k$ , are believed to be all the more important as factors associated with qualitative changes in the sintered materials.

In this report, production experiments were conducted regarding more extensive calcination temperatures with the same methods as in the previous report in order to clarify this point. Changes in calcined contraction rates and resistivity of sintered materials due to calcination temperature were studied as were the effects of calcination temperature on resistance of the powdered state of carbon black. These were correlated and studies were attempted of the mechanism of change in resistivity of sintered materials based on calcination temperature

## 2. Experimental method

The materials used were carbon black with low resistivity (Tokai Electrode, furnace black, HAF grade, granular form) and commercial Korean kaolin. Properties of the material, methods of production of experimental scraps and methods of calcination in carbon etc. are omitted since they were related in detail in a previous report<sup>2]</sup>.

Tubular samples 6 mm in diameter and 20 mm in length containing 0-15% carbon black were calcinated at 800-1400°C as required and were held for one hour at temperatures in the range of 20-100°C. In addition, powdered samples of carbon black as well as carbon black powder mixed with 15% desiccant were packed in sintering aluminum crucibles and calcination heating treatment was conducted under the same conditions as in the case of the tubular samples.

The sintered material obtained was subjected to silver terminal treatment and the resistance of that was measured as was the resistance of a free accumulation of calcined powder. The measurement methods are the same as previously mentioned and so are omitted.

### 3. Experimental results

#### 3.1 Changes in contraction rate due to calcination temperature

Figure 1 illustrates the change in contraction rate of sintered material versus the calcination temperature. The contraction rates of materials whose carbon admixture proportions are beyond those shown in the figure fit in in a regular fashion with these and there are no special points of notice. For comparison, the calcination in air results of kaolin are included.

The courses of contraction due to calcination are basically uniform but some difference does appear at 1200-1400°C. Specifically, in all samples, at 800°C calcination temperature, 2% initial contraction is observed due to results of dehydration of bound water at 500°C.

Further, at 1000°C, contraction based on destruction of the metakaolin structure appears while at 1100°C, the commencement of major contraction beginning with porcelain formation appears due to vitrification and mullite precipitation. However, in samples containing sintered carbon black in the carbon, this porcelain formation contraction begins at 1160°C which differs from porcelain formation contraction in air. Further, at 1400°C calcination, axial expansion occurs in kaolin calcined in the air.

In carbon sintered material, there is no expansion when the admixture rate of carbon black is low but when the admixture rate exceeds 8%, the expansion gradually increases which is a unique point. Further research is necessary into the causes of these changes but these changes are believed to have some sort of relation with changes in resistivity of sintered materials due to calcination temperature.

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### 3.2 Resistivity of sintered materials

#### 3.2.1 Changes in resistivity due to calcination temperature

Figure 2 illustrates a plot of the resistivity of all experimental samples versus direct calcination temperatures at levels below 100 kΩ. The effect due to calcination temperature is striking when the admixture rate of carbon black is below 4% and is comparatively slight when the rate exceeds 5% and this is believed to be due to the different ranges of carbon granules differentiated by their contact states, as stated in previous reports.

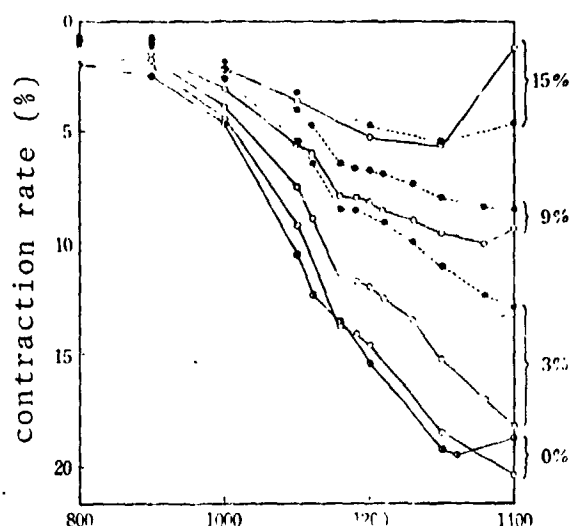


Figure 1. Relation of calcination temperature to calcination contraction rate

calcination temperature ( $^{\circ}\text{C}$ )

The carbon admixture rates are 15%, 9%, 3% and 0%.

-○-: axial direction

-●-: longitudinal direction (for sintered material in carbon)

-◊-: axial direction versus material sintered in air

However, there are numerous common stages between the decrease in resistivity of the various admixture samples and the rise in temperature. Specifically, when the temperature exceeds  $900^{\circ}\text{C}$ , an acute reduction in resistivity appears which abates temporarily at  $1160-1220^{\circ}\text{C}$  and then becomes acute again and then gradually moderates up to  $1400^{\circ}\text{C}$ . Especially in samples with carbon black in excess of 7%, the resistivity of materials sintered at  $1400^{\circ}\text{C}$  rises.



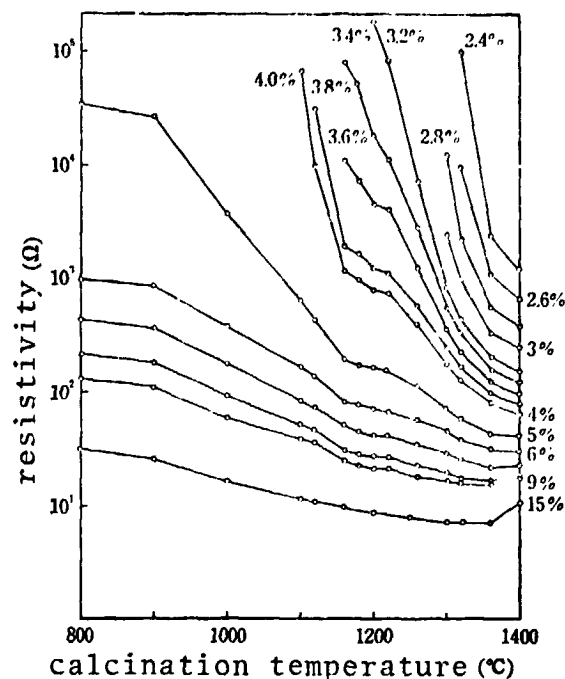


Figure 2. Relation of calcination temperature to sintered material (% in figure represents carbon admixture rates)

A comparison of the stages of resistivity decrease due to calcination temperature with the stages of calcined contraction of figure one illustrates a correspondence relation. Specifically, the stages of resistivity decrease mentioned above correspond to abatement of contraction at 1200°C and at 1100°C as well as 1000°C and also to expansion seen in samples containing more than 8% carbon black at 1400°C.

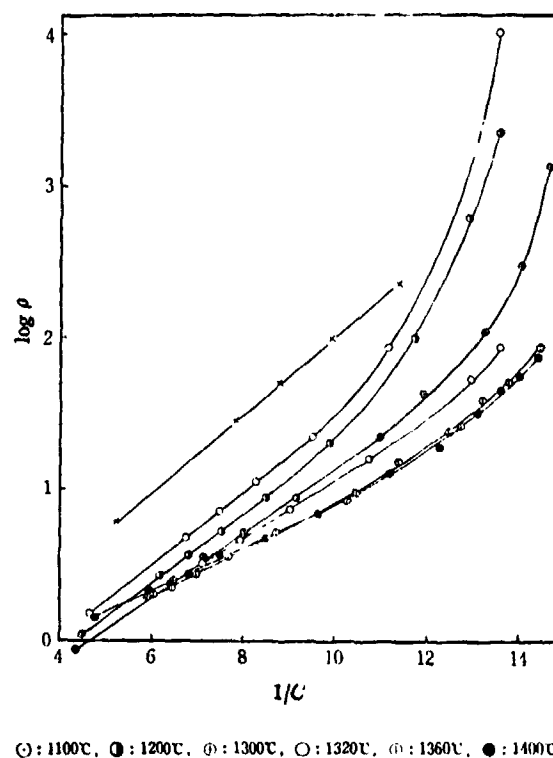


Figure 3. Relation of carbon bulk density to comparative resistivity (x:non-calcined sample)

3.2.2 Relation of carbon bulk density to specific resistivity. Conducting the same calculations as in the previous report, the comparative resistance ( $\rho$ ) as well as the carbon bulk density ( $C$ ) of the sintered material were found for the above samples and plots of  $\log \rho$  to  $1/C$  were made. The results, as reported in previous reports, were that a linear relation not cut at low resistivity regions was attained for all calcination temperatures up to 1300°C.

There was little change in the slopes  $\rho^2$ . However, as illustrated in figure 3, clear changes in the slopes appear when the calcination temperature exceeds 1300°C. The constants A and k change greatly in the relation  $\rho = Ae^{k/C}$ . At low temperatures where the slope does not change greatly, there should be something corresponding to a qualitative change with the transition gradually to the low resistivity side of this linear relation due to calcination. However, the changes at temperatures above 1300°C signify additional qualitative changes.

In order to clarify the aspect of these qualitative changes due to calcination temperature, a curve of  $\log \rho$  versus  $1/C$  as in figure 3 is drawn for each calcination temperature. By means of these,  $\log \rho$  versus fixed C was found by interpolation and this  $\log \rho$  was plotted versus the calcination temperatures. These results are illustrated in figure 4. By some mechanism, the resistivity intrinsically decreases with rise in calcination temperature. In this resistivity reduction curve, correspondence to each stage of the contraction curve is found, albeit slight. In addition, when temperatures exceed 1200°C, acute resistivity decrease is evident especially in high

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<sup>2</sup> Detailed examination of the slopes shows they are not constant up to 1300°C. They show slight reduction with rise in temperature. This is related to compression stated subsequently.

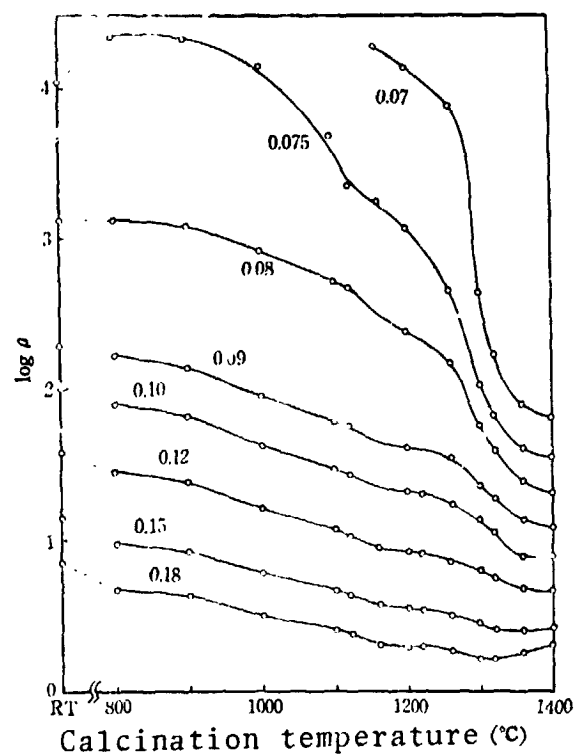


Figure 4. Relation of calcination temperature to specific resistance (Numbers in figure are g/ml bulk density of carbon).

resistivity regions.

3.3 Resistivity changes of structural components due to calcination.

3.3.1 Resistivity of free accumulation state of carbon black

It has been clearly indicated in a previous report that the resistivity of the free accumulation state of carbon black is directly related to the resistivity of carbon black-kaolin sintered material.

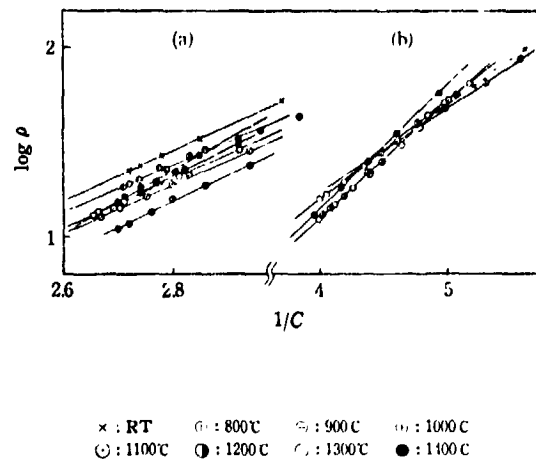


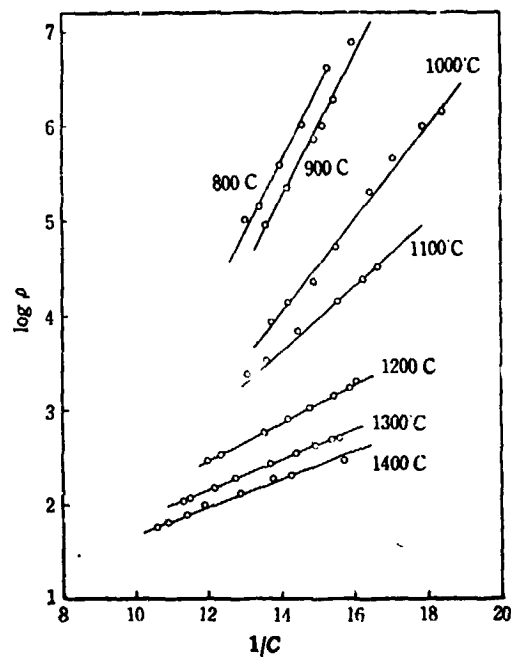
Figure 5. Free accumulation state resistivity of calcine treated carbon black.

(a) Calcine treated commercial material

(b) Material derived from crushing (a) and passing it through an 80 mesh screen.

Accordingly, it is easy to imagine that qualitative changes due to heating of carbon black are influenced by resistivity reductions due to calcination temperature. When these changes are great, there is a possibility that other more basic effects will taper off and become unclear. In this experiment, furnace black with low resistivity was selected for use. Accordingly, while the influence of heating changes on carbon black itself are not believed to be too great, the degree of influence must be determined.

Figure 5 (a) illustrates the measurements of heat treated commercial powder. The reciprocal of the bulk density and the specific resistance are in a virtual linear relation. The positions and slopes are slightly influenced by the calcination temperature.



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Figure 6. Free accumulation state of calcine treated compound powder.

Specifically, non-treated materials indicate the highest resistivity with resistivity decreasing as the calcination temperature rises. The lowest value is reached at 1200°C and it tends to increase further as the temperature rises. In the carbon black used in the experiments, some bound hydrogen remains in the vicinity of the carbon hexagonal ring network and if we assume that it is released, this would account for the decline in resistivity of the sintered material in figure 4. However, the change is most small in comparison with compound. Since the effects of distribution state of powder, granulation and destruction are necessary in consideration of the resistivity of the free accumulation state of powder, measurement was first conducted and the heated carbon black was then crushed in mortars, passed through 80 mesh screens

and finally, measurement of the resistivity of the free accumulation state of powder was conducted. As illustrated in figure 5 (b), there are slight differences depending on the degree of pulverization but distinction between groups was virtually impossible. The results indicate that the changes in quality of the carbon black used in the experiment due to calcination treatment were very slight. and were not of the same magnitude as the changes in resistivity due to calcination of the sintered material.

### 3.3.2 Resistivity of carbon black-kaolin compound powder

In the compound state, the effects due to calcination vary. In anticipation of effects such as mutual reactions at high temperatures, desiccant with 15% carbon content was pulverized and the resistivity of the free accumulation state of powdered samples calcinated at various high temperatures was studied. In order to eliminate effects of granulation of sintered material, the powder was pulverized after calcination and passed through 80 mesh screens. The measurement results are illustrated in figure 6. The horizontal axis in the figure is modeled after the case of sintered material. Approximations are found according to the following formula. This axis is the reciprocal of (C), the carbon bulk density per unit area of free accumulation state.

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$$C = \frac{W}{1 - \frac{W}{100} \times \frac{15}{100}} \times \frac{\pi}{4} d^2 h$$

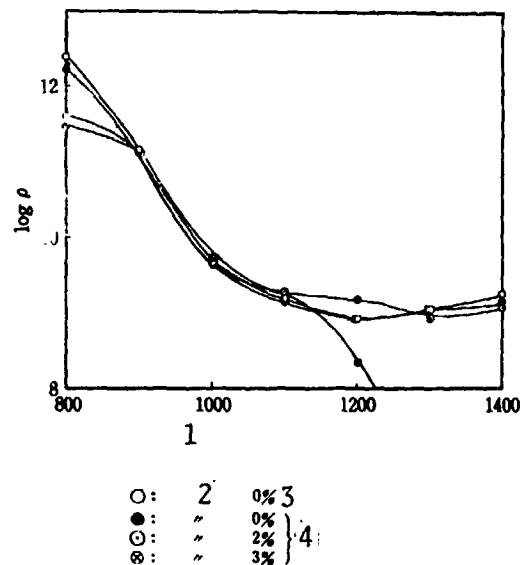


Figure 7. Relation between insulation resistivity of sintered material and calcination temperature

- key
1. calcination temperature (°C)
  2. rate of compound carbon
  3. material calcined in air
  4. material calcined in carbon

The measurement voltage is 1000V, the measurement temp. 200°C.

Here  $W$  is the weight of the calcined powder charged in glass tube with  $d$  inner diameter to  $h$  height while  $\Delta W$  is rate of weight reduction due to calcination of powder containing 15% carbon. The results of measurement of compound plastic material were used. Table 1 illustrates this  $\Delta W$ . While  $\Delta W$  may have some variation between sintered and powdered material, consideration of reactive combustion loss of carbon during the course of calcination indicates that this  $C$  does not precisely illustrate the carbon bulk density in powder.



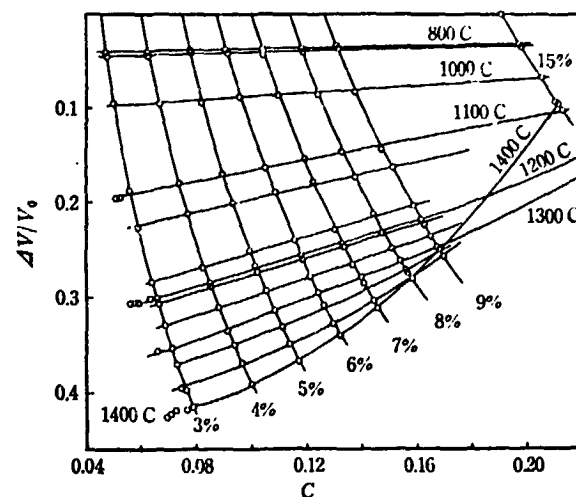


Figure 8. Relation of C to  $\Delta V/V_0$

(Figures indicate carbon content and calcination temperature)

However, the changes of the value of  $\Delta W$  in table 1 show no significant disparity due to calcination temperature. In approximate comparisons of mutual relations among powders or with sintered materials, a suitable index is the carbon content.

| Calcination temp. (°C) | 800   | 900   | 1000  | 1100  | 1200  | 1300  | 1400  |
|------------------------|-------|-------|-------|-------|-------|-------|-------|
| $\Delta W$             | 0.087 | 0.088 | 0.094 | 0.096 | 0.095 | 0.098 | 0.102 |

Table 1. Rate of calcined weight reduction of sintered material with 15% carbon admixture rate

The results of figure 6 obtained in this way indicate that the resistivity of compound powders differs considerably from that of pure carbon black and that the resistivity declines markedly with calcination temperature. Since the carbon bulk density range has  $1/C$  exceeding 11, it is proportionate to intermediate resistance of a compound.

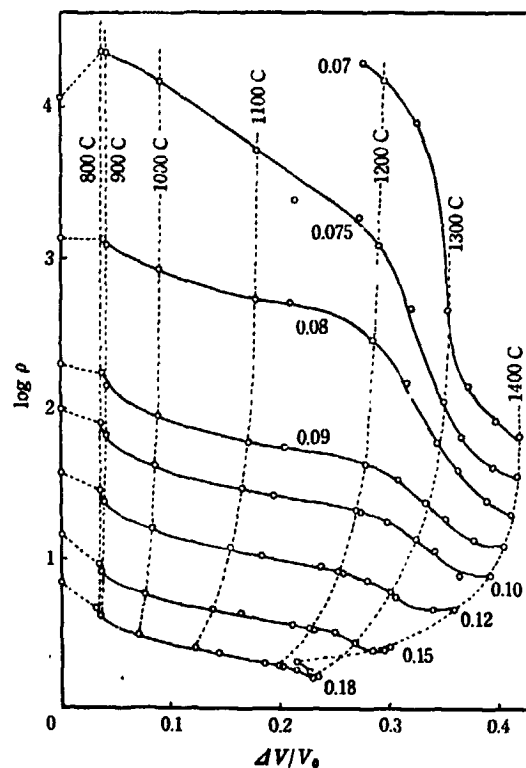


Figure 9. Relation of specific resistance to calcination contraction rate (fixed carbon bulk density)

The resistivity changes closely resemble the case of  $1/C > 11$  from figure 3 and there is a close relation with resistivity changes of the compound. However, since the powder is composed of fine grains, there is a great possibility that the individual grains are fine, sintered bodies and they need not show changes of structural components.

### 3.3.3 Insulation resistivity of kaolin sintered material

Up to a calcination temperature of 1300°C, the resistivity of sintered material with a carbon content of up to 2% is the same as that of pure kaolin oxidized and calcined in air with measurement at 200°C. Previous reports have indicated that there is virtually no effect of carbon admixture or strong reduced calcination in carbon.

In this experiment, results of measurement of insulation resistivity of calcined material at 1400°C in which changes in slope in the log p versus 1/C relation arose, were virtually identical up to 1300°C so that there actually was no change.

Figure 7 indicates the insulation resistivity of sintered material up to 3% carbon admixture rate. It shows considerable decline with rise in calcination temperature up to 1200°C. However, all kaolin sintered material in air were the same. This does not indicate that in material sintered in air, this decline due to calcination temperature is a resistivity change intrinsic to the material. Believed due to the porosity, there is virtually no possibility of change arising in resistivity intrinsic to volume in sintered material, at least in kaolin decomposition material.

### 3.4 Relation of specific resistance to volume contraction rate

#### 3.4.1 Relation of log p to $\Delta V/V_0$ compared at fixed carbon bulk density

Since the above results indicate that there is not much contribution of resistivity changes of structural components themselves as calcination temperature influences, the cause of qualitative change of resistivity decrease based on calcination temperature in the case of fixed bulk density of sintered material carbon shown in figure 4 must be found elsewhere. Thus, note is taken of the fact that there is correspondence at each stage of the contraction curve although slight. These were very regular with no experimental error. Accordingly, changes such as decline in resistivity with rise in calcination temperature

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are probably related more to contraction than to calcination temperature. Thus, a relation is sought with the volume contraction rate as the horizontal axis instead of the calcination temperature.

It is not possible to directly find the volume contraction rate ( $\Delta V/V_0$ ) at each calcination temperature versus a fixed sintered material carbon bulk density (C). Thus the curve of  $\Delta V/V_0$  versus C is first drawn with parameters of carbon admixture rates and calcination temperatures (Fig. 8). Interpolating for a fixed C from this figure, the  $\Delta V/V_0$  values found for each calcination temperature are plotted versus each point of  $\rho$  of figure 4. These results are illustrated in figure 9 in which the entire plot is always a smooth curve with no stages remaining at the calcination contraction points. This indicates not only that calcination contraction reduces resistivity values as a result of increasing the carbon bulk density of sintered materials but also involvement in reduction of resistivity values by a separate method.

These qualitative contractions due to contraction are explained as follows. Specifically, examination of the sintered contraction curves of figure 1 shows clearly that the calcination contractions of the compounds are based in virtually all cases on kaolin sintering. As a result, examination of carbon black proportionate to the free accumulation state distributed in the compound as bulk shows that compulsory compression occurs with sintering of kaolin and not spontaneous sintering contraction.

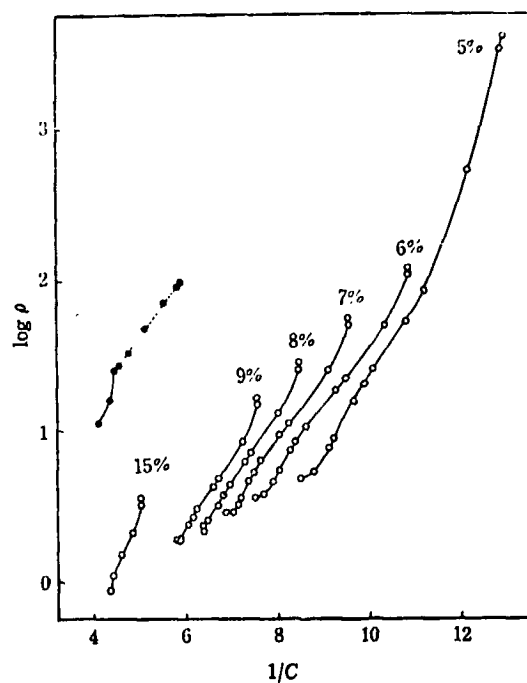


Figure 10. Resistivity changes due to compression and calcination.

key ○: sintered material (% is carbon admixture rate)  
 ●: Carbon black free accumulation state (dotted line is only right-left striking while solid line is upward-downward oscillation).

Thus, the carbon granules give rise to deviation proportionate only to the pressure from mutual contact proportionate to the free accumulation states. This is believed to appear as an influence of calcination temperature.

#### 3.4.2. Relation of $\rho$ versus $\log (V/V_0)$

[REDACTED]

In a previous report, in measurement of resistivity of the free accumulation state of carbon black, a straight line of  $\log \rho$  versus  $1/C$  was obtained through lateral striking and lateral deflection was witnessed through the addition of upward-downward impact which indicates that the sample powder underwent partial compression. Figure 10 is a plot of the carbon admixture rate versus the relation of  $\log \rho$  versus  $1/C$  of sintered material and also illustrates the free accumulation state resistivity of carbon black. The relation of  $1/C$  change due to calcination with resistivity change is very similar to the relation of  $\rho$  versus  $1/C$  in the case of upward-downward shaking in powder resistivity.

There have been numerous reports of resistivity changes with natural or man-made graphite due to pressurization of carbon powder. There have been reports of resistivity being proportionately related to  $1/P$  ( $P$  pressurized from without)<sup>3]</sup> as well as proportionate relations with  $1/\sqrt{P}$ <sup>4]</sup>. In addition, Takahashi<sup>5]</sup> reports that depending on the type of carbon black, it is proportionate to either  $1/P$  or  $1/\sqrt{P}$ . Material with comparatively low resistivity is said to have a proportionate relationship with  $1/\sqrt{P}$ .<sup>§ 3</sup>

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§ 3 The author has also conducted the same experiments. The powder resistivity of carbon black used in this experiment was confirmed to be proportionate to  $1/\sqrt{P}$ .

While the same sort of relation is anticipated with sintered material, pressurization in this case cannot be directly measured and controlled. In the event of contraction by calcination from dried state volume  $V_0$  to  $V$ , the contact state of carbon black in the sintered material is in a state of compression to  $V$  by pressure  $P$  from capacity  $V_0$  proportionate to the free accumulation state. If we take as  $K$  the apparent compression rate of carbon black at this time, then  $dV/dP=KV$ . Here  $K$  may not be constant. Generally, because it is a function of  $P$ , if we take  $K=k_c P^{m-1}$  ( $k_c$  and  $m$  are constants) and integrate the pressure when  $V=V_0$  as  $P_0=0$ , then

$$P = -\frac{m}{k_c} \left( \ln \frac{V}{V_0} \right)^{1/m} \quad (1)$$

This signifies that  $\log (V/V_0)$  can serve as an index of the pressure added to the carbon particles in sintered material.

When the general relation of pressure and resistance of powder is taken as  $\rho = A/P^n + B$ , then because  $\rho$  becomes very small with increase of  $P$  in carbon black, consideration of the resistance scope of the compound results in  $B=0$ . Accordingly, the following is the result of expressing pressure as volume contraction.

$$\rho = A \left( \frac{k_c}{m} \right)^n \left( -\log \frac{V}{V_0} \right)^{-n/m} \quad (2)$$

or

$$\log \rho = \text{const} - \frac{n}{m} \log \left( -\log \frac{V}{V_0} \right)$$

Below is an examination of the mutual relation of the experimental results based on these relations.

First, it is possible to directly plot from calculations of experimental results the relation of  $\log p$  and  $\log (-\log \frac{V}{V_0})$ , when the calcination temperature is in a parameter, for a sample with a fixed carbon admixture rate. The results are illustrated in figure 11. Each plot is fairly straight up to a calcination temperature of 1120°C. The slope  $n/m$  is about one up to a carbon admixture rate of 6%. However, there is some bulge and there are some depressions in the plot and the slope decreases with rise in the admixture rate. The values of the slope found from the figure are illustrated in table 2.

| Carbon admixture rate (%) | 5    | 6    | 7    | 8    | 9    | 15   |
|---------------------------|------|------|------|------|------|------|
| Slope $n/m$               | 2.26 | 1.25 | 1.08 | 0.98 | 0.84 | 0.74 |

Table 2. Slope of linear portion of figure 11.

Next, figure 12 illustrates the same relation with a fixed sintered material carbon bulk density. With  $C=0.08$  g/ml or less, a linear relation is attained up to 1200°C just as in figure 11. Moreover, in this case, the slope  $n/m$  is about 1/2. The  $n/m$  values found from the figure are illustrated in table 3.

Since the pressure dependence of the compression rate  $k$ , specifically the value of  $m$  is unclear, a definite conclusion is difficult to reach. If the apparent compression rate of carbon black in compound were fixed (In the measurements conducted on powdered carbon black by Takahashi <sup>5)</sup>,

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this was in the range of 15-120 kg/cm<sup>2</sup>), m=1 would result.  
The slopes of tables 2 and 3 illustrate directly the values  
of n.

| Carbon bulk density (g/ml) | 0.075 | 0.08 | 0.09 | 0.10 | 0.12 | 0.15 | 0.18 |
|----------------------------|-------|------|------|------|------|------|------|
| Slope n/m                  | --    | 0.54 | 0.53 | 0.54 | 0.50 | 0.45 | 0.40 |

Table 3. Slope of linear portion of figure 12.

Specifically, in this case, p is proportionate to 1/P  
in the former and is proportionate to 1/√P in the latter.  
However, the capacity change arising as a result of  
contraction is due both to deformation of granules and to  
granular migration and realignment. In formula (1), if  
capacity change were to occur due only to deformation of granules,  
m=1 would result while if such change were exclusively due  
to positional movement, m would approach zero. Specifically,  
m is believed to exhibit the ratio of granular deformation  
versus capacity change. Accordingly, with a fixed carbon  
admixture rate, this effect must of course be considered.  
If  $\rho \propto 1/\sqrt{P}$  were valid in the compound, the compression  
rate based on contraction versus collection of carbon black  
in compound would not be fixed and m would have to be  
0.5.

#### 4. Considerations

4.1 Theoretical considerations of resistivity changes due  
to contraction

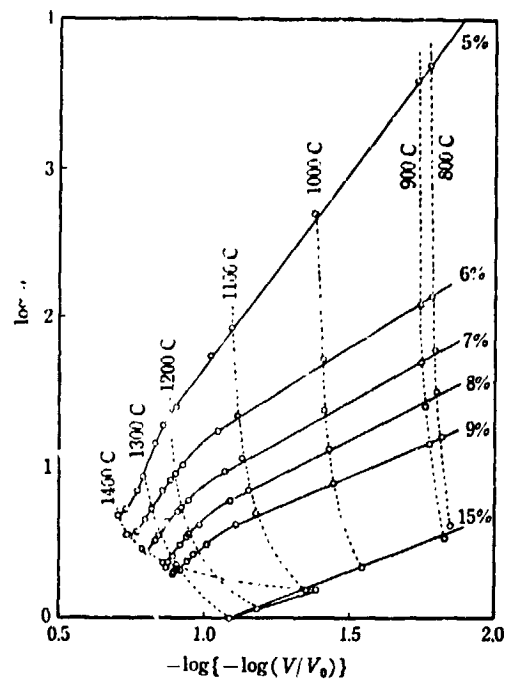


Figure 11. Relation of  $\rho$  to  $\log(V/V_0)$  (fixed carbon admixture rate).

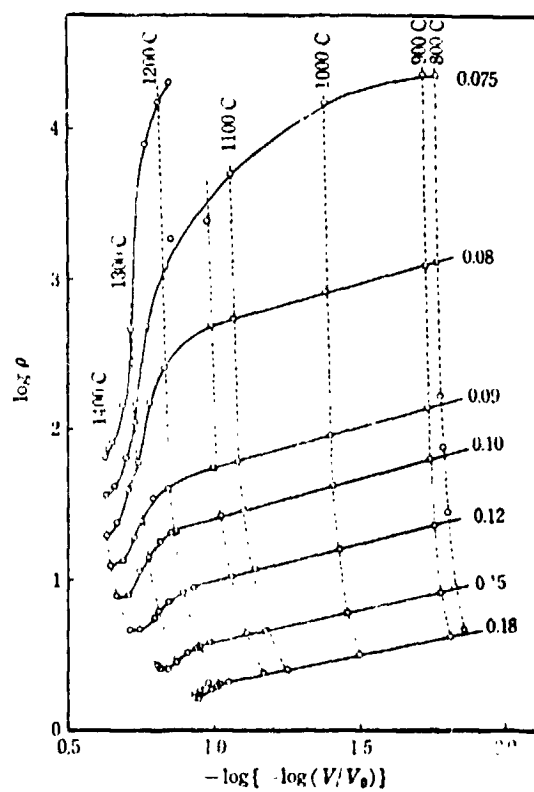


Figure 12. Relation of  $\rho$  to  $\log(V/V_0)$  (fixed carbon bulk density).

Generally, when the conductor granules are in contact, contact resistance is classified into concentrated resistance based on the relatively small size of the contact point and into barrier resistance due to impurity dilution of the boundary face of the contact segment. Considering from both sides the concentration resistance of material with  $\rho'$  specific resistance in contact at a small circle with radius  $a$ , since  $r = 2 \times \rho' / 4a$  is calculated, if the barrier membrane specific resistance is taken as  $\rho''$ , the resistance of one contact portion would be expressed as <sup>6]</sup>

$$r_c = \frac{\rho'}{2a} + \frac{\rho''}{\pi a^2} \quad (3)$$

In the case of carbon black, the individual granules are oriented tangentially to the numerous, fine carbon hexagonal ring plates on the surface. Since the width of the individual plates is approximately  $20 \text{ \AA}$  <sup>7]</sup>, it is proportionate to  $1/20 - 1/25$  of the granule diameter (approximately  $0.05\mu$ ). Approximately 2000 individual plates are aligned on the surface. Accordingly, on the average, contact between the granules will take place on the level portion of the plates. This level portion is pure in comparison with peripheral tips and in contact in sintered material, the contact boundary surface undergoes heating and pressurization, eliminating ever more impurities. Since the barrier resistance can be expected to become sufficiently low, item 2 in formula (3), in comparison with item 1, can be assumed to become sufficiently small.

Specifically,  $r_0 = k' \rho' / a$  ( $k' = \text{const}$ ).

If we take the number of average points of contact in the contact region as  $m_c$ , the contact resistance per contact region would be  $r_p = r_c / m_c$ . The  $r_p$  has a  $[\Omega]$  dimension and not a direct relation with the amount of carbon. Thus, in the formula  $p = Ae^{k/C}$ , the resistance in distribution proportionate to the free accumulation state of carbon black may be considered to be a variable included in A. Specifically,

$$\rho = A' r_p e^{k/C} = A' \frac{k' \rho'}{m_c a} \cdot e^{k/C} \quad (4)$$

The pressure versus given mass of carbon black in the compound is affected by the resistance passing through  $m_{c0}$  and a. If we assume that this contact portion is under pressure p, the following applies.

$$p = \pi a^2 m_c F_p \quad (5)$$

Here  $F_p$  is a transformation coefficient of carbon black granules which may be assumed to be constant within a narrow pressure range. With carbon black having low resistivity such as that used in the experiments, considering the surface structure mentioned previously, the contact area a is assumed to vary with pressure and since  $m_c$  may be considered to be a constant close to 1, the following formula is derived from formulas (4) and (5).

$$\rho = K \rho' e^{k/C} \cdot \frac{1}{\sqrt{p}} \quad (6)$$

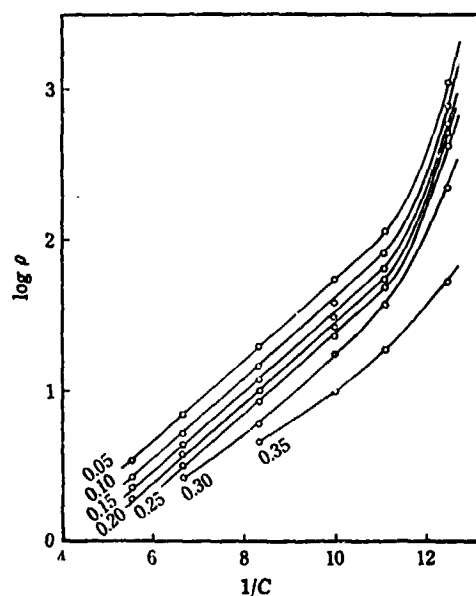


Figure 13. Relation of  $\log p$  to  $1/C$  compared with  $\Delta V/V_0$  fixed. (Numbers in the figure are  $\Delta V/V_0$ )

$K$  here is constant.

If we assume that  $k$  is not affected by compression, then  $p$  and  $C$  can be considered independently in relation to the resistivity of sintered material. Specifically, when the pressure is constant, the specific resistance  $p$  is determined only by the distribution and loading state of the granules and the formula illustrates the relation of carbon bulk density  $C$  with  $\log p \propto 1/C$ . When the carbon bulk density  $C$  is constant, the dependence on the relation of  $p \propto 1/\sqrt{n}$  based on change in contact resistivity between granules is indicated.

However, this  $p$  is pressure at one contact region. Note should be taken of the difference from  $P$  versus concentration in formula (1). When we consider that the capacity change due to calcination contraction is  $m < 1$  because of granular movement due to porosity decrease,  $p$  is expected to have a more direct relation with  $P$ .

$$p \propto -\ln\left(\frac{V}{V_0}\right) \quad (7)$$

Accordingly, formula (6) becomes

$$p = K' p' \cdot 1/C \left(-\ln \frac{V}{V_0}\right)^{-1/2} \quad (8)$$

This relation no doubt is in conformity with the results of figure 12.

The fact that the slope in the straight line (Fig. 3),  $\log p$  versus  $1/C$  when the calcination temperature is constant, declines slightly with rise in calcination temperature is not in contradiction with the hypothesis that  $k$  is fixed regardless of the pressure. Rather, when the calcination temperature is fixed, since the contraction rate  $\Delta V/V_0$  differs with the carbon bulk density  $C$  (Fig 8), the linear relation when the calcination temperature is fixed ought to differ somewhat from the linear relation when the pressure is fixed. Using figure 9, when a plot is made of the relation  $\log p$  versus  $1/C$  using interpolation when  $\Delta V/V_0 = \text{constant}$ , figure 13 is derived. This result signifies that the linear regions are virtually parallel with  $k/2.3 \approx 1/3.7 = \text{constant}$ .

From these formulas,  $e^{k/C}$  corresponds to change in the number of contact points of the carbon black granules while  $1/\sqrt{p}$  corresponds to change in the contact area at the contact point. As a result, the fact that  $k$  for change of pressure is constant signifies that the relation to the number of contact points is determined only by  $C$  and is not related to  $p$ . Specifically, as for changes of  $C$  due to capacity change, the portion originating in compression of the granules themselves is small which is the same as considering that due to compression, the granules migrate, realign themselves and fill the void.

Accordingly, figure 11, the changes due to calcination contraction of the specific resistance when the carbon admixture rate of the compound is fixed, may be considered as being due to changes in carbon bulk density  $C$  due to migration of granules and to changes in contact pressure of granules with granules in an equilibrium state. The  $1/\sqrt{p}$  of carbon black and the basic relation corresponding to  $1/p$  should not be considered as direct indicators. Based on formulas (7) and (8), calculation of slope  $n$  for a fixed carbon admixture rate results in

$$n = -\frac{d \ln \rho}{d \ln p} = \frac{1}{2} + \frac{k}{C^2} \cdot \frac{dC}{d \ln p}$$

Since  $C = C_0 / (V/V_0)$ , this and formula (7) result in

$$\begin{aligned} -\frac{dC}{d \ln p} &= \frac{\frac{dC}{d(V/V_0)}}{\frac{d \ln p}{d(V/V_0)}} = \frac{-\frac{C_0}{(V/V_0)^2}}{-\ln(V/V_0) \cdot \frac{1}{(V/V_0)} + \frac{1}{(V/V_0)^2}} \\ &= C \left( -\ln \frac{V}{V_0} + \frac{1}{2} \left( \frac{V}{V_0} \right)^2 \right) \\ \therefore n &= \frac{1}{2} + \frac{k}{C} \left\{ -\ln \frac{V}{V_0} + \frac{1}{2} \left( \frac{V}{V_0} \right)^2 \right\} \end{aligned} \quad (9)$$

Specifically,  $n$  is not a constant but is affected by the carbon bulk density  $C$ . As  $V$  decreases with compression, it is expected to gradually increase from  $1/2$ . The following calculations of  $n$  result through entry of measurements of experimental sintered material into formula (9). Considering only the linear relation of  $\log p$  and  $1/C$ ,  $C=0.2-0.1$ . Since the  $k/2.3$  in the case of fixed pressure is  $1/3.7$ ,  $k/C=3.1 - 6.2$ . Further, in the region corresponding to the linear portion of figure 11,  $\Delta V/V_0=0.05 - 0.20$ . Accordingly, when the carbon bulk density  $C$  is large, the approximate size of  $n$  is

$$n \sim 0.5 + (0.05 \sim 0.22) \times 3.1 \sim 0.66 \sim 1.18, \text{ average } 0.92.$$

Further, when  $C$  is small,

$$n \sim 0.5 + (0.05 \sim 0.22) \times 6.2 \sim 0.81 \sim 1.86, \text{ average } 1.43.$$

These calculations are in general agreement with the experimental results of figure 11 and table 2.

Thus, regardless of two or three assumptions, formulas (6) and (8) coincide in experimental results and the resistance relation of sintered material is generally indicated. When the carbon admixture rate is fixed,  $C$  and  $p$  vary only with contraction so that formula (6) is represented as follows by means of variable  $(V/V_0)$ .

$$\rho = K' \rho' e^{\frac{1}{2} \frac{V}{V_0}} \left( -\ln \frac{V}{V_0} \right)^{-1/2} \quad (10)$$



If carbon bulk density C was used,

$$\rho = K' p' e^{K''/C} \left( \log \frac{C}{C_0} \right)^{-1/2} \quad (11)$$

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Here K' is a constant.

#### 4.2 Summary of effects of calcination temperature

By the above experimental results and considerations, the resistance of sintered material in low resistance ranges with comparatively great carbon bulk densities is expressed by formulas (6), (10) or (11) at least up to 1200°C. If the intrinsic resistance p' of carbon black granules does not change greatly due to calcination, these formulas indicate that the effect due to calcination temperature will depend almost exclusively on calcination contraction. This is a most important conclusion in respect to the problem of yield which has been a past concern in production of this type of resistor. Specifically, in previous reports, material calcined at 1200°C was reported to have excellent reproducibility of resistivity and little variation and the cause clearly lies in the retardation of contraction near 1200°C which appears in calcination contraction curves illustrated in figure 1. This in turn is due to the use of substrate porcelain with little calcination contraction or substrate porcelain with little change in calcination contraction in the range of calcination temperatures. This suggests the possibility of marked increase in industrial yields.

However, the experimental results also clearly indicate that a separate effect must be considered with regard to calcination temperatures above 1200°C when the carbon bulk density is very low.

Since the intermediate resistance range in which the carbon bulk density ( $C$ ) is low is a range in which the carbon granules gradually become isolated, the changes in  $C$  due to calcination contraction cause not only increase in contact points due to rearrangement of granules but also increase in contact points due to reduction in isolated granules. Specifically, in this range, a rapid reduction of  $p$  occurs beginning with contraction. This is indicated by the relation of  $1/C$  to  $\log p$  of the carbon admixture rate of 5% from figure 10 and corresponds to the extreme size of  $n/m$  when the carbon admixture rate is 5% as in figure 11 and table 2. Since these are related to the number of contact points,  $e^{k/C}$  in formula (6) signifies an influence beyond carbon bulk density  $C$ . The idea that when  $c$  is smaller than a certain fixed value,  $k$  is no longer constant but increases with reduction of  $C$ , suggests a relation between this intermediate resistance range and formula (6).

When the temperature exceeds 1200°C, a separate influence appears in relation to resistance. For example, in figure 12, the relation of  $\log\{-1/g(V/V_0)\}$  to  $\log p$  from 1200°C indicates the appearance of an influence outside of contraction with separation from the straight line and a downward depression with rising temperature.

[REDACTED]

Further, when a temperature in excess of 1300°C is reached, the large size of carbon bulk density indicates a tendency to another upward curve. These may also be considered as being linked with changes in constants such as  $K$ ,  $p'$  and  $k$  in formula (6). However, in the experimental results, the free accumulation state resistivity of pure carbon black was little influenced by calcination treatment. In addition, the volume intrinsic resistance of kaolin sintered material up to 1400°C is virtually unaffected even in the event of sintering in contact with carbon. Accordingly, at high temperatures, it is necessary to take into consideration changes in the distributive loading state of carbon granules based on factors other than contraction. However, at temperature above 1360°C, in connection with the clear changes in the linear relation of  $1/c$  to  $\log p$  of figure 3, perhaps the idea of some chemical reaction among carbon-kaolin decomposition materials is appropriate. A temperature for initiation of reaction of graphite and oxide for  $\text{SiO}_2$  at 1 atm would be 1460°C but in a pure vacuum, it would be 1250°C. With fireproof clay, it would be even lower, 1100°C in a pure vacuum<sup>8]</sup> so that there seems to be sufficient possibility of a surface chemical reaction of a magnitude great enough to alter the electrical resistance of a compound. Further reports are planned regarding the effects of changes at these high temperatures.

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